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ANTIOXIDANT ACTIVITY OF SWEET PRODUCTS WITH ANTHOCYANINS EXTRACTS USE AS A NATURAL FOOD COLORANT

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Summary. Consumers are increasingly avoiding foods containing synthetic colourants, which lead food industries to replace them by natural pigments, such as carotenoids, betalains, anthocyanins and carminic acid. The objective of this research was to elucidate the influence of the substitution of synthetic colorants (carmoisine) with extracts of grape anthocyanes on the organoleptic, physico-chemical and antioxidant properties of some confectionery products (marmalade, jellies).

Key words: Antioxidants, natural colorants, grape seeds anthocyanins, confectionery products.

One of the major hazards of this beginning of the millennium is the larger use of various synthetic food additives. Firstly, it includes synthetic colorants, which are present practically in most types of processed food. The danger is even greater when it comes to children who consume, having a small body weight, a mass of sweets, brightly colored, so the contribution of additives per kg of body weight is often dangerous to health, causing various allergic reactions.

Recently, natural plants have received much attention as sources of biologically active substances including antioxidants, antimutagens and anticancers [1]. Plant extracts obtained from some fruits and vegetables have been reported to be effective antioxidants. In most cases, phenols mediate their anticancer effects by inhibiting all stages of chemical carcinogenesis, initiation, promotion and progression as well as formation of carcinogens from dietary precursors.

Grape (*Vitis vinifera*) is one of the world's largest fruit crops, while grape seed is a complex matrix containing approximately 40% fiber, 16% oil, 11% proteins, and 7% complex phenols including tannins, in addition to sugars, mineral salts, etc. Proanthocyanidins of grape seed are a group of polyphenolic bioflavonoids, which are known to possess large pharmacological activities and therapeutic potentials [2,3]. Proanthocyanidins, the major polyphenols found in red wine and grape seeds, have been reported to show cardio protective effects against ischemic reperfusion injury. In addition, grape seeds are rich sources of monomeric phenolic compounds, such as (+)-catechins, (+)-epicatechin, (+)-epicatechin-3-o-gallate, and, dimeric, trimeric and tetrameric procyanidins, which have antimutagenic and antiviral effects. Recognition of such health benefits of catechins and procyanidins has facilitated the use of grape seed extract as a dietary supplement [4].

The objective of this research was to elucidate the influence of the substitution of synthetic colorants (cramoisy) with extracts of grape anthocyanes on the organoleptic, physical-chemical and antioxidant properties of some confectionery products (marmalade, jellies).

MATERIALS AND METHODS

Spectrophotometer measurements were performed by UV–Vis spectrophotometer **Pye *Unicam UV4-100 UV-Visible***.

The study group was made a jelly quartz cell size of 10 x 10 mm (working volume of 4 ml), which was placed in the sink-holder device. The measuring process starts automatically after closing the sample compartment (= 546 nm).

The method of determining the ability of inhibiting oxidation activity of hydrogen peroxide (HPSA - hydrogen peroxide scavenging activity).

The ability to inhibit the activity of hydrogen peroxide oxidation (HPSA) is determined according to the method published in NAGULENDRAN et al., 2007 [5].

The principle of the method. The ability to recover hydrogen peroxide is determined by titration method of substitution (the test solution does not come into direct reaction so transformed into a chemical compound, which is then titrated with a solution of known concentration).

Reagents: hydrogen peroxide H2O2 (0,1 mM), a solution of ammonium molybdate (NH4) 6Mo7O24 • 4H2O (3%), sulfuric acid, H2SO4 (2M), sodium thiosulfate Na2S2O3 (5,09 mM), potassium iodide KI (1,8 M), concentrated nitric acid, HNO3, distilled water [5].

EXPERIMENTAL RESULTS

Production of jelly products can not only be considered as a combination of the mechanical action of raw materials. During cooking there is a series of very important physical and chemical changes, which to some extent affect the bioavailability of the raw materials used and the finished product. When cooking, always follow the technology and production conditions in order to get a finished product that meets the quality requirements specified in the regulations, and exhibits antioxidant properties.

Preservation of color - an important indicator of the quality of the product manufactured from natural dye. Change the color speaks of the destruction of natural dyes, which reduces the nutritional value of the product.

Given these conditions it has been determined the optimum pH at which the maximum intensity of the color is preserved and the optimum temperature at which the anthocyanins may be introduced into the product, avoiding their destruction. For marmalade optimum value is the range of pH 2.5-2.7, and the optimum temperature + 60 ° C.

The measurements were performed using a spectrophotometer UV/vis "UNICAM", length 1 cm cuvette at wavelength = 546 nm. The results are presented in figure.1.

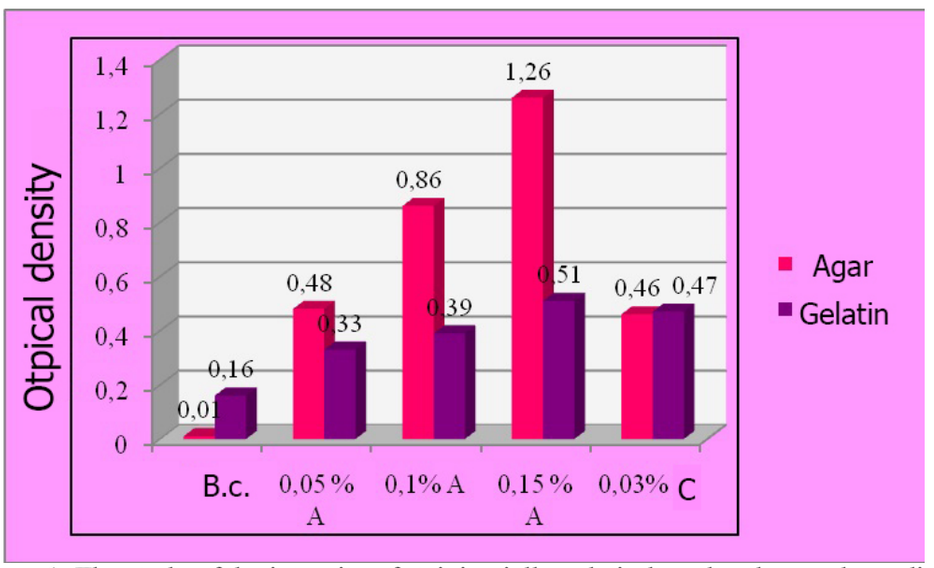

Figure 1. The study of the intensity of staining jelly gelatin-based and agar, depending on the nature of the dye

The study of intensity jelly products, depending on the nature of paint shows that gelatin products with natural paint color intensity is less than the intensity karmuazinom jam on synthetic gelatin. The intensity color by adding 0.05% anthocyanins equals 0.33 units and adding synthetic karmuazina intensity equal to 0.47 units. For the agar jelly also the color intensity of the product by adding 0.05% solution is almost the natural dye intensity karmuazine sample (0.48 and 0.47, respectively). Thus, marmalade, made on agar with natural dye has a higher color intensity than jam on gelatin. When adding the synthetic dye to the color intensity of the two samples is almost the same marmalade 0.46 and 0.47 units. For the agar jelly, based on natural dye intensity range is between 0.48 1.26 units and for marmalade on gelatin - between 0.33 0.51 units depending on the number of added anthocyanin.

The concentration of anthocyanin affect color intensity can be considered on *figure 2*.

The intensity of the color of jelly products on gelatin and agar grows with increasing concentration of added anthocyanin. Maximum color intensity is observed when adding 0.15% anthocyanin - 0.51 units of samples on gelatin and 1.26 units of samples on agar. The intensity of the color of the samples on agar are 1.5-2.5 times higher than that of samples in gelatin. This can be explained by the fact that initially (even without dye) the marmalade on agar jelly is a colorless product but marmalade on gelatin has a yellowish color. Therefore, the addition of the dye to the samples on the basis of gelatin, dims out the color of marmalade, and the color intensity of the product falls.

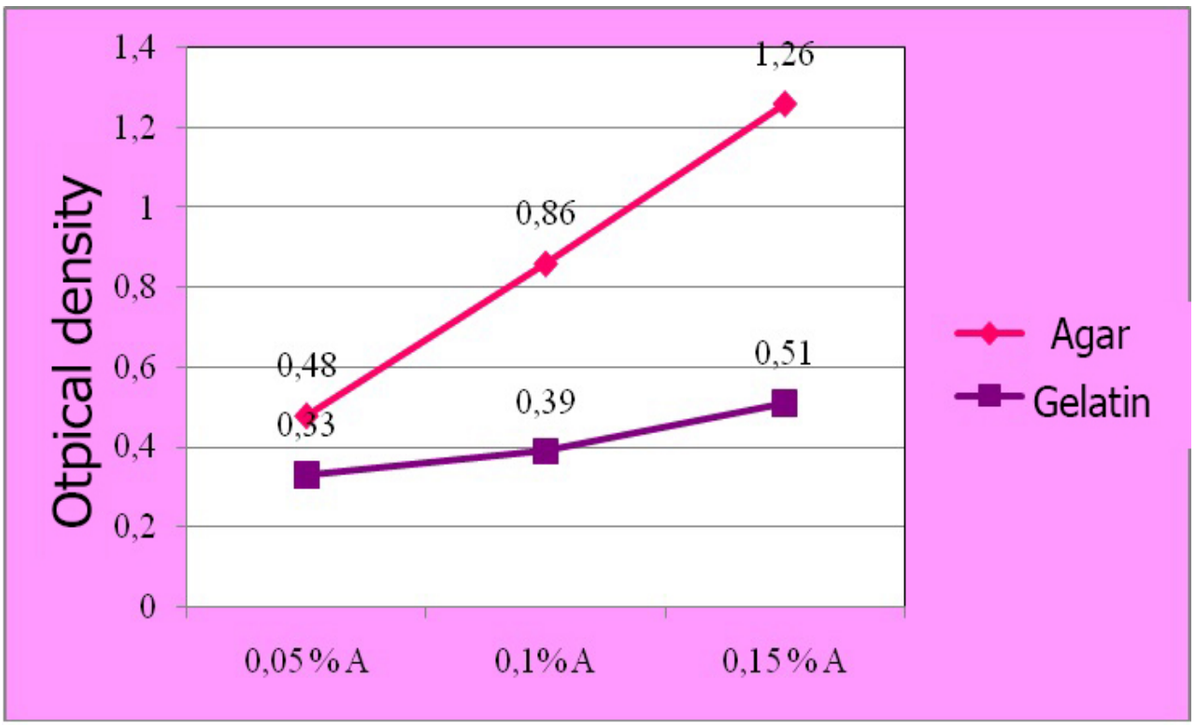

Figure 2. The study of the intensity of the colors of jelly products depending on the concentration of anthocyanin that were added to the product.

The color intensity is a composite index, which depends on a combination of factors: the nature of the dye, natural ingredients and the concentration of the dye. In order to more accurately describe the intensity of the color of the product is necessary to consider the impact of each factor separately.

Study of changes in the color stability during storage

Anthocyanins - are plant pigments whose color depends on the acidity of the medium. At pH <6 anthocyanins are red variable intensity, more vivid and more dense at pH 1-2, at a pH of 6 - violet at a pH of 8 - blue at pH = 10 - green. Color intensity increases with decreasing pH, thus adding citric acid items increases color stability.

It was found that the acidity of the investigational product is pH = 2.5. In order to determine the color stability over time it has been defined the intensity of the colors of jelly products on the day of manufacture and after 15 days of storage. The measurements were performed in the laboratory on photocolorimeter at wavelength = 540nm. The results are presented in figure 3.

The intensity of the color jelly product within 15 days varies slightly. The color of jelly products based on synthetic dyes does not change.

More clearly it can be represented the change of the intensity of the color of jelly products in the diagrams. It can observe changing the the color stability over time, depending on the nature of the dye, the nature of ingredients and the qualiy of natural dyes.

Undesirable property of natural dyes is to reduce the color of the product during storage. Regardless of the nature of the ingredients in both cases, the products with natural dyes decrease the color intensity of the product for 15 days. But this reduction is not as significant. In the study jelly products reducing the intensity does not exceed 0.04-0.06 units.

If in samples with natural dyes color intensity decreases, then in the specimen with a synthetic dye color intensity of the product over time will not change at all. In jelly products prepared on the basis of gelatin it is observed the greatest decrease of the intensity by 0.05 units (at 0.05% content of anthocyanin). The highest intensity of staining characteristic of agar jelly, where the color intensity equals 1.26 and in storage decreases by only 0.03 units.

Thus, the products of synthetic dyes can be considered more stable. But the use of natural dyes is very important due to their many favorable properties. In addition, the charts data suggest that if a product is made of natural dyes concentration of 0.15% or higher, the intensity will decrease slightly.

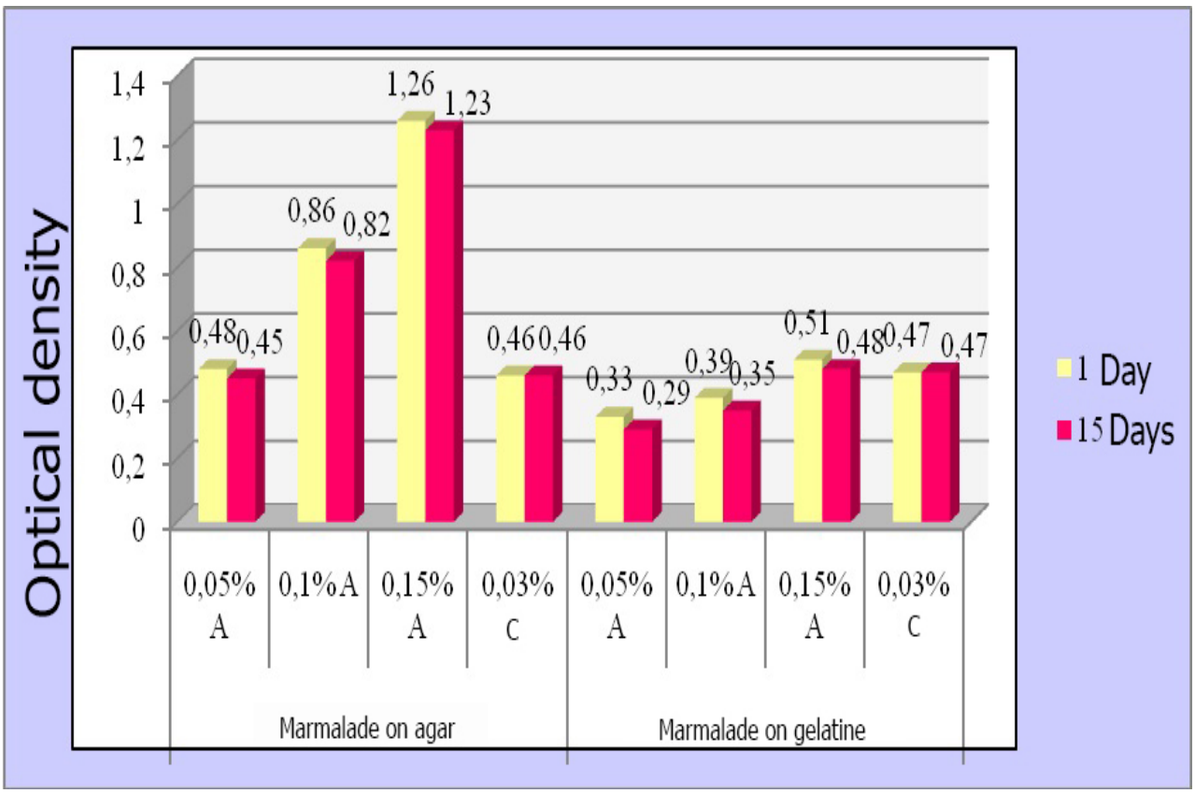

Figure 3. Changing the color stability of jelly products in time depending on the nature of the dye and natural ingredients.

Determination of the inhibition of oxidative activity of hydrogen peroxide. Many fans of sweet like jelly products (lemon drops, chewing marmalade). Jelly products (lemon drops, chewing marmalade) like many fans of sweet. Their unusual taste pleases kids and adults. Jam and jelly decorate cakes and desserts, ice cream and biscuits. It is very important that of all the sweets the marmalade is the most useful. The fact is that it includes nutrients such as agar-agar, pectin, gelatin and applesauce.

Agar-agar is a product of plant origin which improves liver. Pectin is a soluble dietary fiber, helps normalize the digestive tract. Marmalade is a low-fat confectionery product; it contains no fat, and therefore is considered a dietary product. It is also widely known that the marmalade is an excellent anti-depressant, as it helps to relieve stress and improve mood.

But most importantly, marmalade can be also an excellent antioxidant, for example, if it is composed of natural dye anthocyanin.

The antioxidant properties of marmalade from natural dye can be determined by the ability to inhibit the action of anthocyanin hydrogen peroxide.

The obtained data are recorded in Table 1.

The nature of the dye has a large effect on the antioxidant properties of the product. In both types of marmalade natural dye products, the antioxidant activity (AOA) of the finished product increases. The higher the concentration of the dye in the product, the higher the antioxidant activity is. Contrary, the synthetic dye may reduce or increase slightly the antioxidant activity depending on the nature of the ingredients.

In the marmalade on agar, not yet painted, initially there is a rather high content of antioxidants, so the addition of anthocyanins, the AOA of products increases significantly with 5.38% in the

unpainted product and to 18.25% in the product, which contains 0.15% anthocyanins.

In the marmalade on gelatin the initial antioxidant content is very low only 1.28%, therefore the highest AOA rises to 11.46% in the richest anthocyanins sample.

Synthetic dyes have an undesirable effect on AOA of the product. The sample on agar synthetic dye reduced AOA by almost 3.5 times from 5.38% to 1.63%.

In this paper, it is important to understand and analyze how and how much natural dye - anthocyanin affected significantly on AOA of the product. To do this, consider the following diagram.

Table 1. The results of the study of antioxidant activity of jelly products

Nr.	Ingredients	The concentration of the dye,%	$\bar{V}_0$	$\bar{V}_1$	$HPSA(\%H_2O_{2inhibat}) = \frac{V_0 - V_1}{V_0} \cdot 100$, %
1.	**Marmalade on agar**	Without dye	4,65	4,40	5,38
2		0,03% crimson	6,15	6,05	1,63
3.		0,05 % anthocyanin	5,20	4,80	7,69
4.		0,1% anthocyanin	5,65	4,90	13,27
5.		0,15 % anthocyanin	6,30	5,15	18, 25
6.	**Marmalade on gelatin**	Without dye	3,90	3,85	1,28
7.		0,03% crimson	5,10	5,00	1,96
8.		0,05 % anthocyanin	4,10	3,90	4,88
9.		0,1% anthocyanin	3,85	3,50	9,09
10.		0,15 % anthocyanin	4,80	4,25	11,46

The AOA of the value marmalade products is directly proportional to the amount added to the product of anthocyanin. With increasing concentration of anthocyanin rises AOA of the product. In both types of jelly products AOA increases by 2.5 times from 7.69% to 18.25% in the products on the agar and 4.88% to 11.46% in products in the gelatin. But regardless of that, marmalade on agar with anthocyanin concentration of 0.15% contains 1.5 times more antioxidants than marmalade on gelatin with the same concentration of anthocyanin. Because in the marmalade on agar initially there is a high level of antioxidants, it can be considered as its antioxidant properties lushimi and jellies more useful.

CONCLUSION

The addition of extracts of grape anthocyanes gave an excellent antioxidant effect on the marmalade compared with the effect of synthetic colorant. In addition, natural antioxidants are safe and impart health benefits to the consumer. Increased knowledge of their bioavailability and therapeutic effects will result in better adoption of anthocyanin-based products as functional foods.

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